

# PATENT SPECIFICATION (11)

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- (21) Application No. 32057/77 (22) Filed 29 July 1977 (19)  
 (31) Convention Application No. 75539 (32) Filed 5 Aug. 1976 in  
 (33) Luxembourg (LU)  
 (44) Complete Specification published 4 March 1981  
 (51) INT. CL.<sup>3</sup> C09D 11/10  
 (52) Index at acceptance  
     C3V AD  
     C3M 120 155 156 200 201 XA  
     C3W 209 221 224 302  
     C3Y A130 B230 B240 B241 F620



## (54) INK COMPOSITION FOR THE PRINTING OF POLYVINYLIC MATERIALS

(71) I, MARCEL HEBBELINCK, a citizen of Belgium, of 3 bis, rue du Moulin, B-1330 Rixensart, Belgium, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the printing of polyvinyl material by means of improved ink capable of being diluted in water or in a mixture of water and alcohol.

The printing of polyvinyl material is at present carried out with the use of a large number of printing techniques in which organic solvents are employed, generally of the ketonic type, particularly methyl-ethyl-ketone.

The use of these solvents calls for special measures to avoid pollution and explosion hazard at the printing works. They are also comparatively expensive products which add considerably to the production costs.

Known types of ink i.e. intended for the flexographic printing of paper comprise of hydro-alcoholic base. These inks, by comparison with those mentioned above, have the advantage of being less expensive and of not necessitating any special measures to avoid explosions. They nevertheless do not enable a stable imprint to be produced on supporting materials consisting of polyvinyl materials.

The purpose of the present invention is thus to provide a process enabling printing costs to be reduced and the risk of explosion to be eliminated by a technique which makes it possible for inks of the type capable of being diluted in water or of the hydro-alcoholic type to be used for printing on supports of a polyvinyl material.

This object is achieved by means of a process wherein a support of polyvinyl material is printed with a composition consisting of a polymer of vinyl chloride or a copolymer of vinyl chloride and vinyl acetate manufactured by the emulsion-polymerisa-

tion process and used in the form of a fine powder or of an aqueous dispersion, said polymer or copolymer being dispersed in an amount of 10—30% by dry weight in an ink dilutable in water or in a mixture of water and alcohol comprising a system of one or more water-soluble binding agents and one or more pigments which do not migrate in the plasticizers present in the supports to be printed, whereafter the printed support is covered with a plastisol film which is subsequently gellified at a temperature of 160—200°C.

The system of binding agents for the ink is preferably a water-soluble acrylic or maleic homopolymer or copolymer or any water-soluble resin commonly used for heliographic, typographic or flexographic printing.

Polymers and copolymers of vinyl chloride are sold for the preparation of plastisol and easily obtainable on the market. The main examples which may be mentioned are the polyvinyl chlorides used for coating in powder form, such as those supplied by the firm of Solvay under the trade mark SOLVIC Type 300, the polyvinyl chloride resins of Type PA 1302 supplied by the firm of Rhone Poulenc, these being copolymers of vinyl acetate and vinyl chloride, as well as the aqueous dispersions of copolymers of vinyl chloride which are sold by the firm of BASF under the trade mark LUTOFAN, Type 100 D.

The products used are preferably free of plasticizers, although in the case of aqueous suspensions the possible presence of internal plasticizers causes no major difficulties.

It is nevertheless important that the particular resin used should be compatible with the final covering film of plastisol and that it should not comprise any plasticizers which present an obstacle in this respect.

The emulsion or the dispersion of this resin in the water-dilutable ink usually has to be given the desired degree of viscosity by means of a suitable diluent, which may

be water or else a mixture consisting of variable proportions of water and alcohol. The quantity of diluent used and its constituents depend on the printing process to be used and on the desired drying speed.

The process to which the invention relates is suitable for the conventional printing methods, whether heliogravure, flexographic printing or typographic printing.

A particular advantage offered by the process to which the invention relates resides in the fact that after the printing and drying have been carried out in accordance with the invention the ink has properties causing it to engage and adhere to the plastic support sufficiently firmly, to enable it to be wound onto spools after being printed. Up to this moment the resin introduced into the ink therefore only functions as a charge, which will amalgamate and combine with the final varnish during the finishing phase. The support can thus be provisionally wound up onto reels in the course of production, a facility which renders the operating cycle extremely flexible.

The process is applicable to the printing of plastics supports suitable for numerous purposes. When it is applied to wall coverings the plastisol film used for the final covering need only be applied at the rate of 4–10 g/m<sup>2</sup>, whereas far higher proportions, of the order of 200 g/m<sup>2</sup>, may prove necessary for floor coverings.

As stated above, the gellification temperature is of the order of 160–200°C but depends first and foremost on the nature of the plastisol film applied. Particularly preference is given to a temperature of the order of 180°C.

The finishing operation, i.e. the application and gellification of the plastisol film, may be performed either separately or simultaneously with an embossing or graining operation by the "hot" method. The gellification imparts to the finished product its physical characteristic of unalterability, which is comparable to those of the best products obtained by the processes of the prior art, combined with the technical advance achieved, i.e. the performance of the operation without recourse to any light solvents liable to cause explosion, the expensive solvent used as a diluent in the already known processes being here replaced by water.

It should also be noted that the process to which the invention relates only uses conventional techniques and apparatus for printing and conversion of the polyvinyl chloride.

The invention also relates to an ink composition dilutable in water or in a mixture of water and alcohol, consisting of a dispersion of a polymer of vinyl chloride or a

copolymer of vinyl chloride and vinyl acetate manufactured by the emulsion-polymerisation process and used in the form of a fine powder, or of an aqueous dispersion, said polymer or copolymer being dispersed in an amount of 10–30% by dry weight in an ink dilutable in water or in a mixture of water and alcohol comprising a system of one or more water-soluble binding agents and of one or more pigments which do not migrate in the plasticizers present in the supports to be printed.

The pulverous polyvinyl chloride resin is advantageously emulsified in the ink as a powder in a proportion of 10–30% by dry weight or in the form of a dispersion in water in a proportion of 10–30% by dry weight.

The pigments used may be of any desired kind. Both organic or inorganic pigments are suitable for use within the scope of the invention, provided they do not migrate in the plasticisers present in the under-layer and in the final layer of varnish.

The introduction of the polyvinyl chloride resin into the ink creates between the support and the surface film the connection which is necessary for the production of a fully satisfactory bonding, which could not be obtained if the resin were not present.

The support of polyvinyl material undergoing the printing process according to the invention may be any type of support used in particular for the covering of floors and walls. This support may itself comprise, on the surface opposite to that used for the printing a backing of any desired nature, either simple or composite, such as a backing of asbestos or glass-fiber in the case of floor covering or of paper in the case of wall coverings.

The term polyvinyl material refers essentially to a polymer or a copolymer of vinyl chloride comprising the plasticisers, the stabilizers, the charges, the pigments etc. which are usual in the conversion of calendered plastic materials.

The invention also extends to the products obtained by the application of the process and by the use of the modified ink according to the invention.

The invention will be described in greater detail by reference to the following example, intended to illustrate the invention.

#### Example

An ink is prepared of which the base is as follows:

- |        |   |
|--------|---|
| 10–40% | of pigments which do not migrate in the plasticizer, preliminarily dispersed in the water;        |
| 40–50% | of acrylic resin capable of being diluted in water or a mixture of water and alcohol, of the type |

represented by the AQUE-HYDE  
(trade-mark) supplied by LAW-  
TER CHEMICAL;

- 10—35% of Water;  
5 10% of alcohol.

This ink is given an addition, while stir-  
ring vigorously, of 10—30% of PVC resin  
of Solvic (trade-mark) type 336 or 367/109  
10 or 20—40% of PVC resin of Lutofan  
(trade-mark) Type 100. This basic ink is  
intimately mixed and can, if necessary, be  
crushed in a ball mill.

The preparation is then given the required  
15 viscosity by the addition of water or by a  
mixture consisting of water and alcohol, in  
order to obtain a viscosity of 20" as  
measured in the Ford vessel No. 4.

The required level of final tonality will be  
20 obtained by the addition of a mixture of  
acrylic resins capable of being diluted in  
water and of PVC resin in a ratio of 10—  
20% of the dry weight of the acrylic resin.

To prevent the formation of foam when  
25 small quantities are being printed, it is of  
advantage to add anti-foaming agents, such  
as

- 2 —3% of isopropyl alcohol or  
30 0.5—1% of anti-foaming agent of the type  
represented by NOPCO 1947 V  
(trade-mark) supplied by the  
DIAMOND ALKALI CO. or  
35 SAG 47 (trade-mark) supplied by  
the UNION CARBIDE CORP.

An improved ink composition of this  
kind is suitable for printing by any con-  
ventional process on a support of vinylic  
40 plastics, which is then given a coating of  
plastisol film, the latter being finally coated  
at a temperature of the order of 180°C.

The percentages in the above example  
refer to weight.

#### 45 WHAT I CLAIM IS:—

1. Process for printing vinylic plastic  
materials wherein a support of polyvinyl  
material as hereinbefore defined is printed  
with a composition consisting of a polymer  
50 of vinyl chloride or a copolymer of vinyl  
chloride and vinyl acetate manufactured by  
the emulsion-polymerisation process and  
used on the form of a fine powder or of an  
aqueous suspension, said polymer or co-  
polymer being dispersed in an amount of  
55 10—30% by dry weight in an ink dilutable  
in water or in a mixture of water and alcohol  
comprising a system of one or more water-  
soluble binding agents and one or more  
60 pigments which do not migrate in the  
plasticizers present in the supports to be  
printed, whereafter the printed support is  
covered with a plastisol film which is sub-  
sequently gellified at a temperature of  
65 160—200°C.

2. Process in accordance with claim 1,  
wherein the system of binding agents for the  
ink is a water-soluble, acrylic or maleic  
homopolymer or copolymer or any water-  
soluble resin commonly used for helio-  
graphic, typographic or flexographic printing.

3. Process in accordance with claim 1  
or 2, wherein the emulsion of the resin in  
the water-dilutable ink is given the required  
degree of viscosity by means of a diluent.

4. Process in accordance with claim 3,  
wherein the diluent consists of water or a  
mixture comprising variable proportions of  
water and alcohol.

5. Process in accordance with any one  
of claims 1 to 4, wherein the printing is  
effected by heliogravure or by flexographic  
or typographic printing.

6. Process in accordance with any one  
of claims 1 to 5, wherein the support, to-  
gether with the impression which it con-  
tains, is provisionally wound onto a reel  
before the plastisol film is applied.

7. Process in accordance with claim 1,  
wherein the gellification temperature is  
about 180°C.

8. Process in accordance with any one  
of Claims 1 to 7, wherein the application  
and the gellification of the plastisol film are  
effected separately from an embossing or  
graining operation which is carried out by  
the "hot" method.

9. Process in accordance with any one  
of claims 1 to 7, wherein the application  
and the gellification of the plastisol film are  
effected simultaneously with an embossing  
or graining operation which is carried out  
by the "hot" method.

10. Ink composition dilutable in water  
or in a mixture of water and alcohol, to be  
used for the printing of polyvinyl material  
as hereinbefore defined, consisting of a dis-  
persion of a polymer of vinyl chloride or a  
copolymer of vinyl chloride and vinyl  
acetate manufactured by the emulsion-  
polymerisation process and used in the form  
of a fine powder or of an aqueous disper-  
sion, said polymer or copolymer being dis-  
persed in an amount of 10—30% by dry  
weight in an ink dilutable in water or in a  
mixture of water and alcohol comprising a  
system of one or more water-soluble bind-  
ing agents and of one or more pigments  
which do not migrate in the plasticizers  
present in the supports to be printed.

11. Ink composition in accordance with  
claim 10, wherein the system of binding  
agents used is a water-soluble acrylic or  
maleic homopolymer or copolymer or any  
resin capable of being diluted in water and  
customarily used for heliographic, typo-  
graphic or flexographic printing.

12. Ink composition in accordance with  
claim 10, wherein the polymer of vinyl  
chloride or copolymer of vinyl chloride and

vinyl acetate is placed in suspension in the ink in the form of a powder.

5 13. Ink composition in accordance with claim 10, wherein the polymer of vinyl chloride or copolymer of vinyl chloride and vinyl acetate is added to the ink in the form of an aqueous dispersion.

10 14. Printed products whenever obtained by the application of the process in accordance with any one of claims 1 to 9 or by the use of the ink in accordance with any

one of claims 10 to 13 for the printing of a support of polyvinyl material.

15 15. Process according to any one of claims 1 to 9, substantially as herein before described.

16. Ink composition substantially as herein described with reference to the example.

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Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1981.  
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY  
from which copies may be obtained.